Organotransition-metal complexes as additives for epoxy resins: 1. Their effects on toughness and morphology of epoxy resins

King-Fu Lin*, Wen-Yung Shu and Tain-Luen Wey
Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 10764, Republic of China

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The toughening effects of chromium and cobalt acetylacetonate ($Cr(acac)_3$ and $Co(acac)_3$) additives on diglycidyl ether of bisphenol A/diethylenetriamine (DGEBA/DETA) and tetraglycidyldiaminodiphenylmethane/diaminodiphenylsulphone (TGDDM/DDS) epoxy resins were investigated and correlated with the changes of their fracture surface morphology. According to fracture tests of their compact tension specimens (CTS), $Cr(acac)_3$ had much higher toughening effects than $Co(acac)_3$. Scanning and transmission electron microscope investigation of their fracture surfaces implied that the epoxy resins incorporated with $Cr(acac)_3$ had more cohesive structure than those incorporated with $Co(acac)_3$ or neat resins. The results have been further supported by gel permeation chromatography and wide-angle X-ray scattering analyses, which revealed that $Cr(acac)_3$ could interact with hydroxy groups in the epoxy networks and reinforced the structure.

(Keywords: complexes; additives; chromium acetylacetonate; cobalt acetylacetonate; epoxy resins; toughness; morphology)

INTRODUCTION

For over a decade, organotransition-metal complexes have been used as catalysts for epoxy resins cured with amine[1], anhydride[2,3] and phenolic[4] curing agents. However, Chen and Shyu[5] have suggested that they could be used as additives for epoxy resins to enhance adhesion to fillers. Stoakley and St Clair[6,7] have also found that, by chemical incorporation of cobalt acetylacetonate ($Co(acac)_3$) into diaminodiphenylsulphone (DDS) curing agent before they were cured with tetraglycidyldiaminodiphenylmethane (TGDDM) epoxy resin, one could increase the flexure strength and fracture toughness of the cured resins, and only slightly decrease the glass transition temperature. According to their patent[6], the process would not affect the density, thermal stability and moisture resistance. It has been suggested that the presumed homopolymerization of epoxy resins by $Co(acac)_3$ might be responsible for the improved flexural strength and fracture toughness[7]. However, little experimental evidence was offered to justify their explanation. Recently, Mijovic[8] has raised the question about the toughening effect of $Co(acac)_3$ on TGDDM and diglycidyl ether of bisphenol A (DGEBA) epoxy resins by showing that their change of critical stress intensity factor in mode I, K_{Ic}, was within the 68% confidence interval of the mean value of the control.

In our previous studies[9], a series of organotransition-metal complexes, such as $Co(acac)_3$, $Cr(acac)_3$, $Mn(acac)_3$, $Ni(acac)_3$, $Zn(acac)_3$, $Zr(acac)_3$, etc., were chosen to evaluate their toughening effects on DGEBA and TGDDM epoxy resins, but only $Cr(acac)_3$ and $Co(acac)_3$ had good solubility in the epoxy resins. The experimental results also showed that $Cr(acac)_3$ had even higher toughening effects than $Co(acac)_3$, and its improvement of toughness was far beyond the confidence interval of the control. In the first part of this study, our objective was to elucidate how the incorporation of $Cr(acac)_3$ and $Co(acac)_3$ affected the toughness and morphology of amine-cured DGEBA and TGDDM epoxy resins.

EXPERIMENTAL

Materials

The DGEBA difunctional epoxy resin used was Shell's EPON 826 with an epoxy equivalent weight (*EEW*) of 187 g mol^{-1}, and the TGDDM tetrafunctional epoxy resin used was Ciba-Geigy MY720 with an *EEW* of 125 g mol^{-1}, determined by titration. Diethylenetriamine (DETA; reagent grade, Hayashi Pure Chemical Industries, Japan) was used as the curing agent for DGEBA, and diaminodiphenylsulphone (DDS; Ciba-Geigy HT976) was the curing agent for TGDDM. Chromium acetylacetonate and cobalt acetylacetonate ($Cr(acac)_3$ and $Co(acac)_3$; Tokyo Kasei Chemical Industries) were used as organotransition-metal complex additives.

Sample preparation

$Cr(acac)_3$ and $Co(acac)_3$ predissolved in methyl ethyl ketone (MEK) solvent were added to DGEBA and TGDDM resins, respectively, in various concentrations. Then, the MEK solvent was removed from the mixtures under vacuum at 100°C for about 24 h until no trace of solvent was detected in the i.r. spectra. The mixtures were

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*To whom correspondence should be addressed

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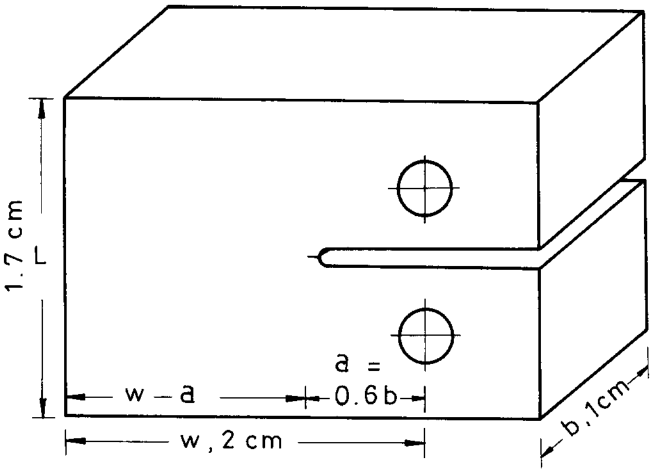

Figure 1 Rectangular compact tension specimen used for fracture test

then analysed by gel permeation chromatography (g.p.c.).

For the DGEBA system, the DETA curing agent was mixed with the $Cr(acac)_3$- and $Co(acac)_3$-incorporated epoxy resins, respectively, in stoichiometric ratio at room temperature. Specimens for mechanical tests were cured at 30°C for 24 h and then post-cured at 128°C for 10 h. For the TGDDM system, the DDS curing agent was added to those incorporated resins in stoichiometric ratio at 120°C, and the mixtures were then stirred vigorously until the grainy solutions turned to homogeneous liquid. Cured specimens were prepared by the following cure cycle: 2 h at 140°C plus 2 h at 177°C plus 4 h at 200°C for post-cure. According to our preliminary tests[9], both cure cycles were able to provide cured DGEBA/DETA and TGDDM/DDS specimens with maximum glass transition temperature (T_g). All specimens after cure were stored in a desiccator at room temperature for at least one week before the mechanical tests were performed.

Analytical techniques

The interaction of $Cr(acac)_3$ and $Co(acac)_3$ with DGEBA monomers was analysed by g.p.c. Some 0.2 g of each mixed sample was dissolved in 10 ml tetrahydrofuran (THF) solvent. Tests were run on a Shodex model RI SE-61 instrument with a mobile-phase flow rate of 1 ml min^{-1}.

The curing exotherm of $Cr(acac)_3$- and $Co(acac)_3$-incorporated epoxy resins with amine curing agents in stoichiometric ratio was measured by differential scanning calorimetry (d.s.c.) performed in a Du Pont model 9900-910 d.s.c. Tests were run at a heating rate of 5°C min^{-1}.

Dynamic mechanical analysis (d.m.a.) of cured specimens was performed in a Du Pont model 983 d.m.a. Tests were run at a heating rate of 10°C min^{-1} and at an oscillation amplitude of 0.1 mm peak to peak.

The fracture toughness of cured specimens was measured by compact tension specimen (CTS) techniques[10]. The mould-cast rectangular CTS specimen is shown schematically in *Figure 1*. A precrack was cut at a temperature about 10°C above T_g of the specimens by using the device suggested in the literature[11]. Fracture tests were performed in an Instron TM tensile tester at a cross-head speed of 0.5 cm min^{-1}. The value of linear elastic strain energy release rate, G_{Ic}, in joules per metre squared ($J\ m^{-2}$), was calculated from[10]:

$$G_{Ic} = YP_c a/Ewb \qquad (1)$$

where P_c = load at crack initiation, a = crack length, E = Young's modulus, w = width of specimen as indicated in *Figure 1*, b = thickness of specimen and Y = geometry factor given by:

$$Y = 29.6 - 186(a/w) + 656(a/w)^2 - 1017(a/w)^3 + 639(a/w)^4$$

The experimental data of fracture toughness, i.e. G_{Ic} value, were averaged from six tested specimens. Their fracture surface morphology was investigated by both scanning and transmission electron microscopies (SEM and TEM). Samples for SEM were gold-sputtered and investigated in a Philips model SEM-515 scanning electron microscope. Those for TEM were prepared by one-stage carbon–platinum (C–Pt) replication of fracture surfaces. A JEOL model JEM-100U transmission electron microscope was used to investigate the fracture surface morphology.

Wide-angle X-ray scattering (WAXS) of the cured epoxy samples was performed on a Philips model PW1710 X-ray diffractometer using Cu K_α radiation and a graphite monochromator. The specimens were cast on the device shown schematically in *Figure 2*. Some of them were pre-cured under rotation at 550 rev min^{-1} until vitrified and then post-cured at 128°C for 10 h, whereas the rest were cured by the regular curing schedule. Diffraction patterns were recorded by scanning at a rate of 3° min^{-1} over an angular range of $3° < 2\theta < 50°$.

RESULTS AND DISCUSSION

DGEBA/DETA epoxy resin systems

Curing properties. Organotransition-metal complexes have long been used as catalysts for curing epoxy resins. Therefore, the catalytic effects of $Cr(acac)_3$ and $Co(acac)_3$, respectively, on curing of DGEBA with DETA in stoichiometric ratio were studied first by dynamic d.s.c. scans. *Figure 3* shows the measured d.s.c. spectra of epoxy resins containing various molar percentages of $Cr(acac)_3$ and $Co(acac)_3$, respectively.

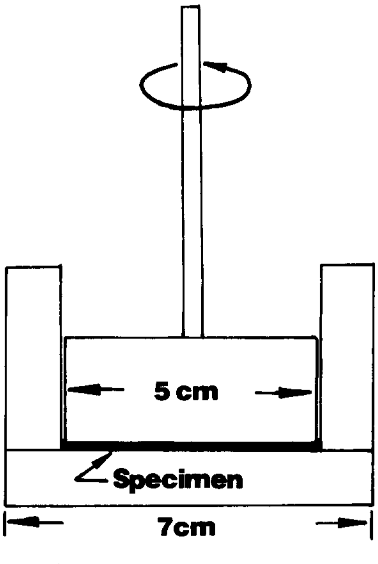

Figure 2 The device used for casting and curing the epoxy specimens for WAXS studies

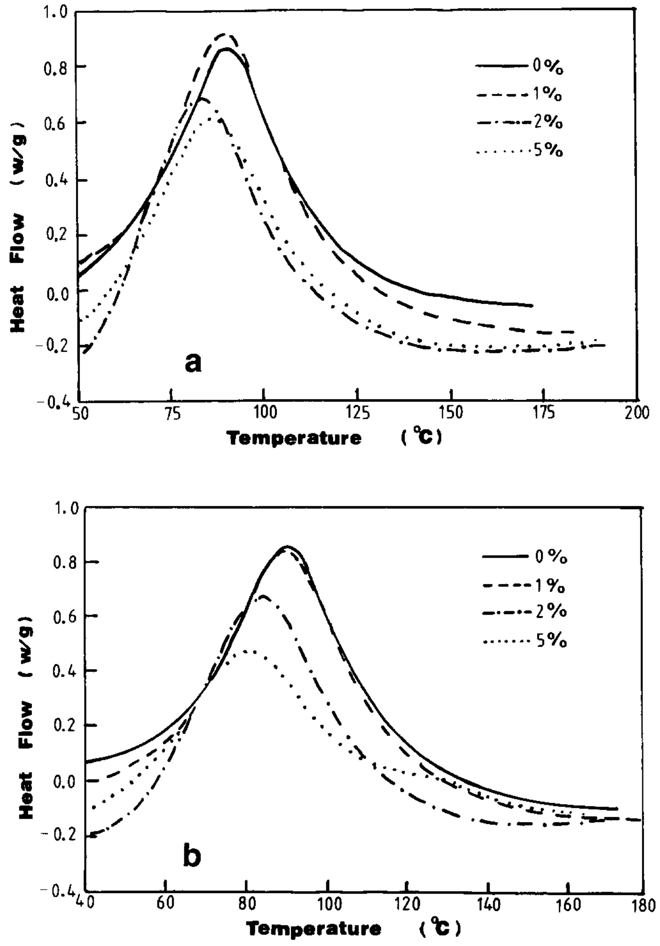

Figure 3 D.s.c. spectra of DGEBA epoxy resins containing various molar percentages of (a) $Cr(acac)_3$ and (b) $Co(acac)_3$, cured with DETA in stoichiometric ratio

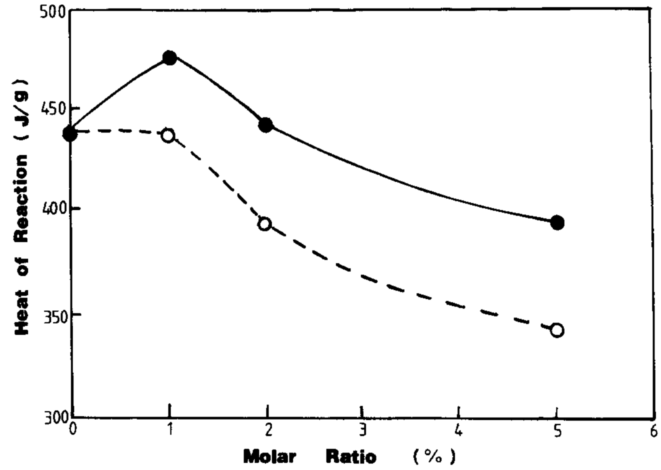

Figure 4 The heat of reaction of modified DGEBA epoxy resins cured with DETA in stoichiometric ratio as a function of molar percentage of incorporated (●) $Cr(acac)_3$ and (○) $Co(acac)_3$

(The molar percentage is calculated by dividing the moles of $Cr(acac)_3$ by the total moles of DGEBA molecules.) The decrease of the temperature of the exothermic peaks with increasing concentration of both $Cr(acac)_3$ and $Co(acac)_3$ shown in the figure indicates that both of them have a catalytic effect on the epoxy resin; the latter has a greater effect than the former. *Figure 4* shows the calculated heat of reaction of modified epoxy resins as a function of molar ratio of incorporated $Cr(acac)_3$ and $Co(acac)_3$. Surprisingly, the heat of reaction of epoxy resin incorporated with 1% $Cr(acac)_3$ is higher than that of neat resin and then decreases with increasing concentration.

The T_g of neat epoxy resin with different curing histories was measured by dynamic mechanical analysis. *Figure 5* shows that their T_g determined from the loss modulus peak in the d.m.a. spectrum was a function of their post-curing time at 128°C after they have been cured at 30°C for 24 h. The specimen reached the optimum T_g after it was post-cured for 10 h; the d.m.a. spectrum of such a specimen is shown in *Figure 6*. The post-cure time of all the specimens, thereafter, was chosen as 10 h. *Figure 7* shows the T_g of modified epoxy resins as a function of molar ratio of incorporated $Cr(acac)_3$ and $Co(acac)_3$, respectively. The highest T_g for the epoxy resin incorporated with 1% $Cr(acac)_3$ might be attributed to its highest heat of reaction. In general, the change of T_g as a function of molar ratio of incorporated $Cr(acac)_3$ and $Co(acac)_3$ roughly followed the trend of heat of reaction shown in *Figure 4*.

Fracture toughness and morphology. The fracture toughness of DGEBA/DETA epoxy resins indicated by strain energy release rate, G_{Ic}, is plotted in *Figure 8* as a

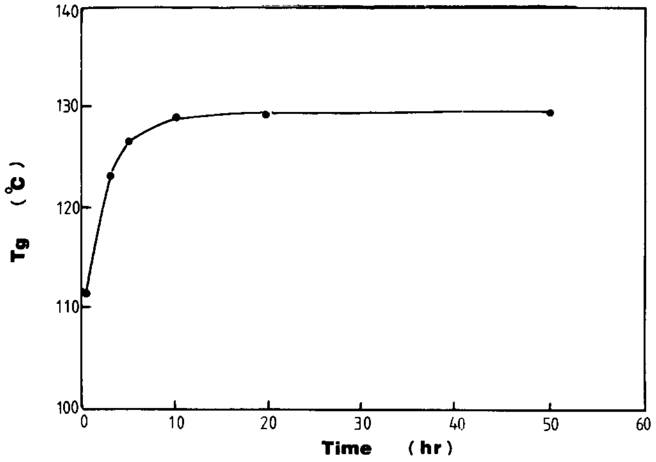

Figure 5 T_g of DGEBA/DETA epoxy resins as a function of their post-cure time at 128°C after they were cured at 30°C for 24 h

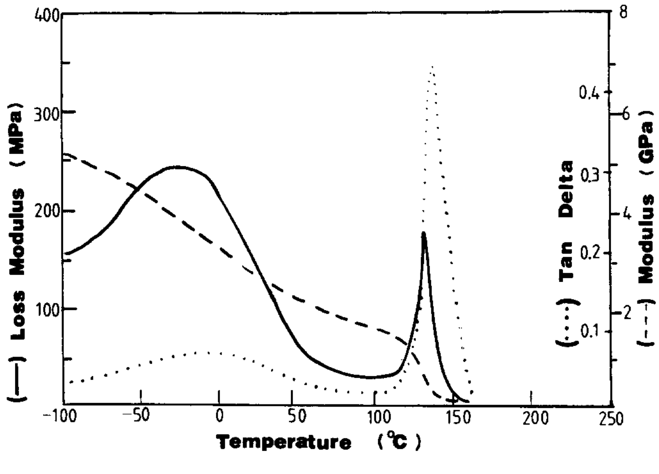

Figure 6 D.m.a. spectrum of DGEBA/DETA epoxy resin after it was post-cured at 128°C for 10 h

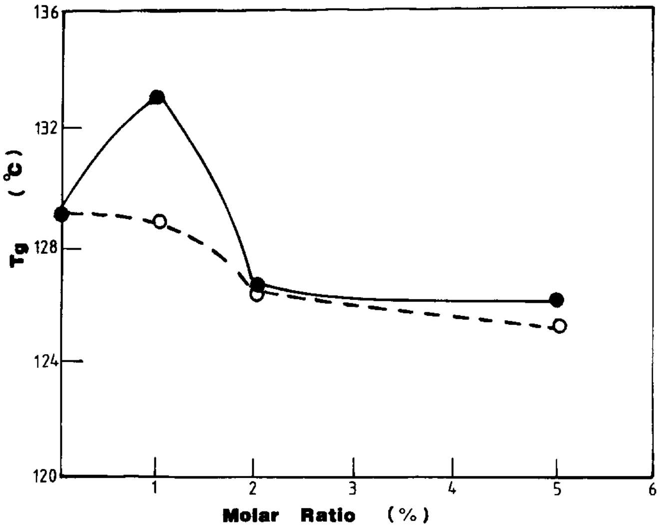

Figure 7 T_g of modified DGEBA/DETA epoxy resins as a function of molar ratio of incorporated (●) Cr(acac)$_3$ and (○) Co(acac)$_3$

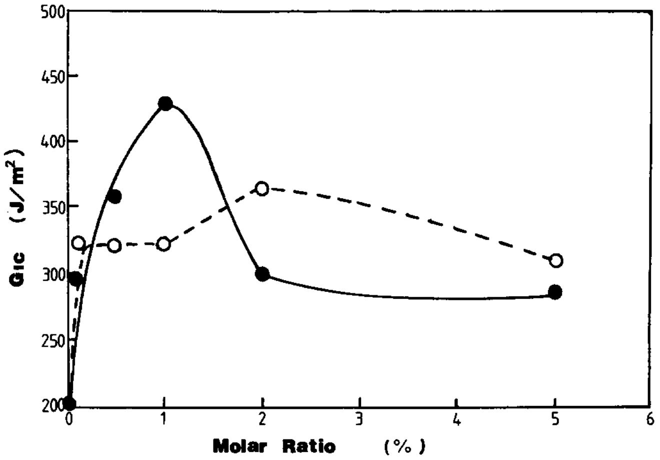

Figure 8 G_{Ic} value of modified DGEBA/DETA epoxy resins as a function of molar ratio of incorporated (●) Cr(acac)$_3$ and (○) Co(acac)$_3$

function of molar ratio of their incorporated Cr(acac)$_3$ and Co(acac)$_3$. As seen in this figure, the epoxy resin incorporated with 1% Cr(acac)$_3$ had the highest fracture toughness, about 110% more than that of neat resin, and hence well above the 68% confidence interval of the mean value of the latter; but the value decreased abruptly as the concentration of incorporated Cr(acac)$_3$ increased above 1%. The epoxy resins containing Co(acac)$_3$ have the highest fracture toughness at 2% molar ratio, about 60% more than that of neat resin, but change in the concentration of incorporated Co(acac)$_3$ did not greatly affect their fracture toughness. In order to explain the toughening behaviour of Cr(acac)$_3$- and Co(acac)$_3$-incorporated epoxy resins, the morphology of fracture surfaces of the specimens was investigated by SEM and TEM electron microscopies.

Figure 9a shows a typical fracture surface of DGEBA/DETA CTS specimens observed by SEM at low magnification. What we were most interested in was the crack initiation region, which covered about 300 μm distance from the crack tip as seen in the magnified picture of *Figure 9b*. Basically, the features of the crack initiation front were affected by local defects produced during the precrack cut, which, in our case, was done by a razor blade immediately after the specimen was heated to 10°C above its T_g. The features changed specimen by specimen, even in the same epoxy formulation. However, the features of the crack initiation region, which showed striations right after the crack initiation front, were quite consistent. The average distance between two adjacent striations was almost constant in the same epoxy samples but changed if their formulations or curing conditions were changed. *Figures 10a–c* show the SEM micrographs of striated zones of DGEBA/DETA, DGEBA/DETA/1% Co(acac)$_3$ and DGEBA/DETA/1% Cr(acac)$_3$ CTS specimens, respectively. It is clearly seen that the striations are marks where the resins were torn off parallel to the crack growth direction. The striations in the DGEBA/DETA specimens were found to be denser than those in the DGEBA/DETA/1% Cr(acac)$_3$ and DGEBA/DETA/1% Co(acac)$_3$ specimens. The distance between two adjacent striations measured from the image in SEM at a magnification of 2500 × by taking the average of 300 data points for each sample is as follows: 3.2 μm for DGEBA/DETA, 4.0 μm for DGEBA/DETA/1% Co(acac)$_3$ and 4.7 μm for DGEBA/DETA/1% Cr(acac)$_3$. The results indicate that the samples with lower fracture toughness have

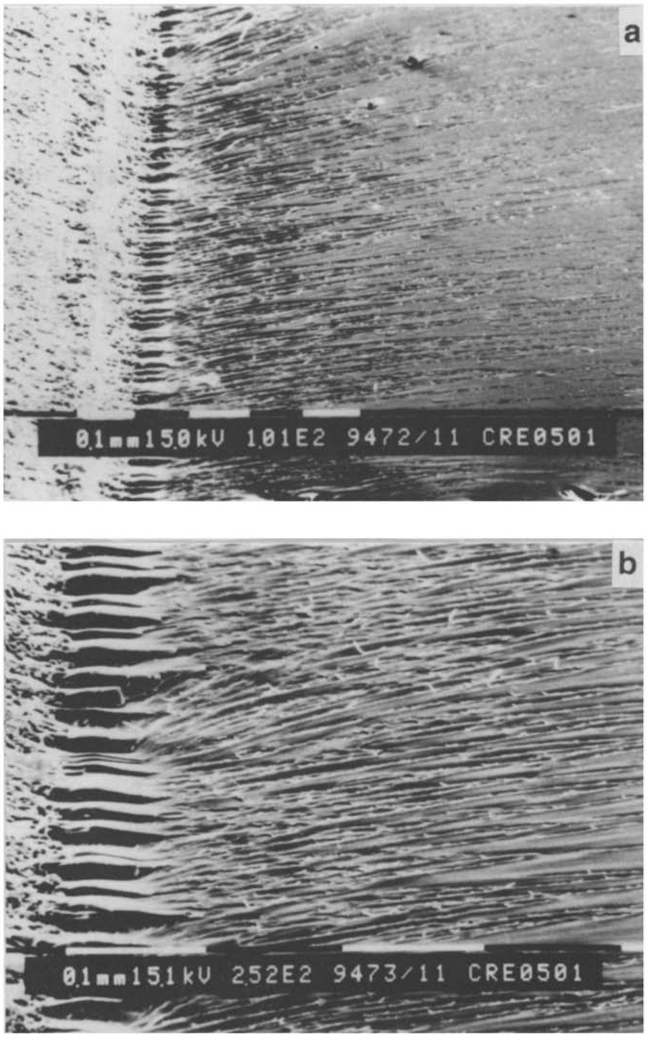

Figure 9 (a) A typical SEM micrograph of a fracture surface of DGEBA/DETA CTS specimen. (b) Magnified picture of (a)

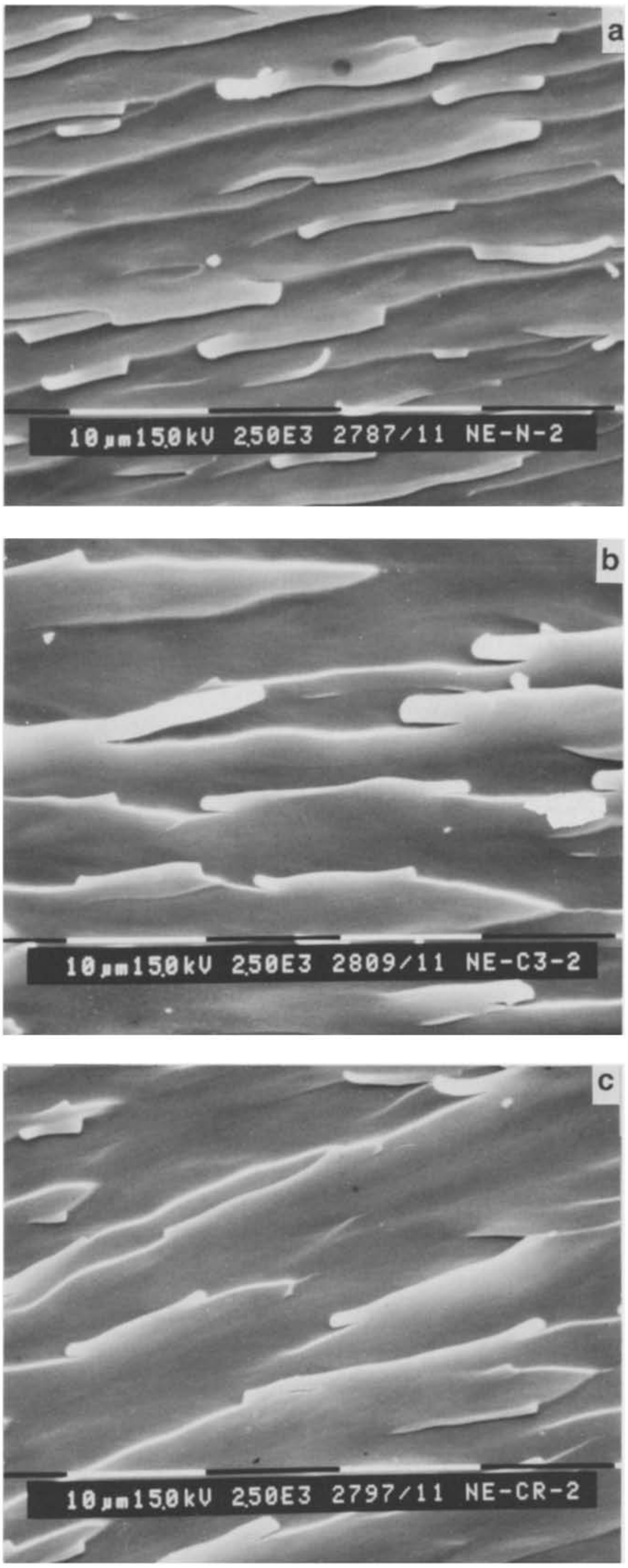

Figure 10 SEM micrographs of the striated zones in the fracture surfaces of (a) DGEBA/DETA, (b) DGEBA/DETA/1% $Co(acac)_3$ and (c) DGEBA/DETA/1% $Cr(acac)_3$

denser striations in the crack initiation region of the fracture surface. A similar result was also reported recently in aromatic epoxy resins toughened with aliphatic epoxy resins[12].

In order to investigate the details of the fracture surfaces, we studied morphologies with transmission electron microscopy (TEM). *Figures 11a–c* show the TEM micrographs of one-stage C–Pt replicas of the fracture surfaces of DGEBA/DETA, DGEBA/DETA/1% $Co(acac)_3$ and DGEBA/DETA/1% $Cr(acac)_3$ specimens, respectively. No significant difference was observed among those three samples. However, after the fracture surfaces were etched with formic acid at room temperature for 1 h, that of the DGEBA/DETA/1% $Cr(acac)_3$ sample was the most severely etched whereas

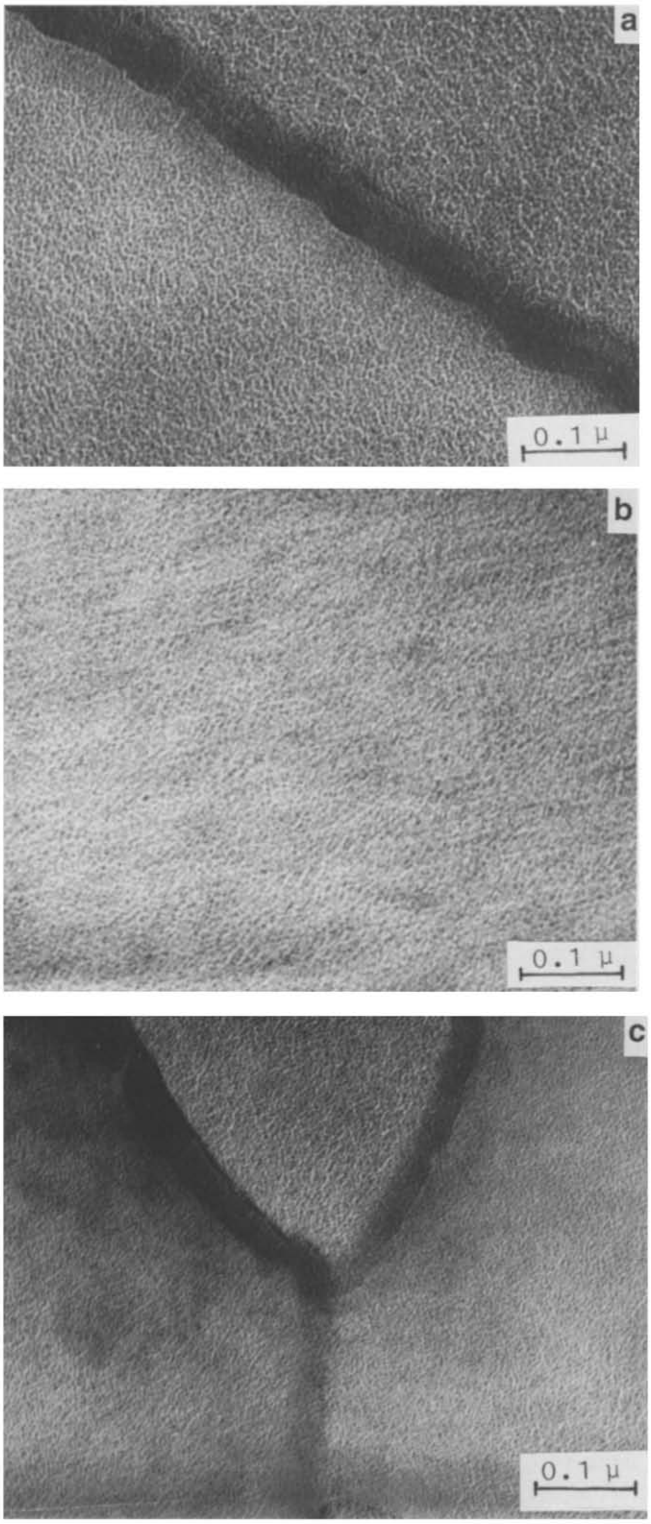

Figure 11 TEM micrographs of one-stage C–Pt replicas of the fracture surfaces of (a) DGEBA/DETA, (b) DGEBA/DETA/1% $Co(acac)_3$ and (c) DGEBA/DETA/1% $Cr(acac)_3$

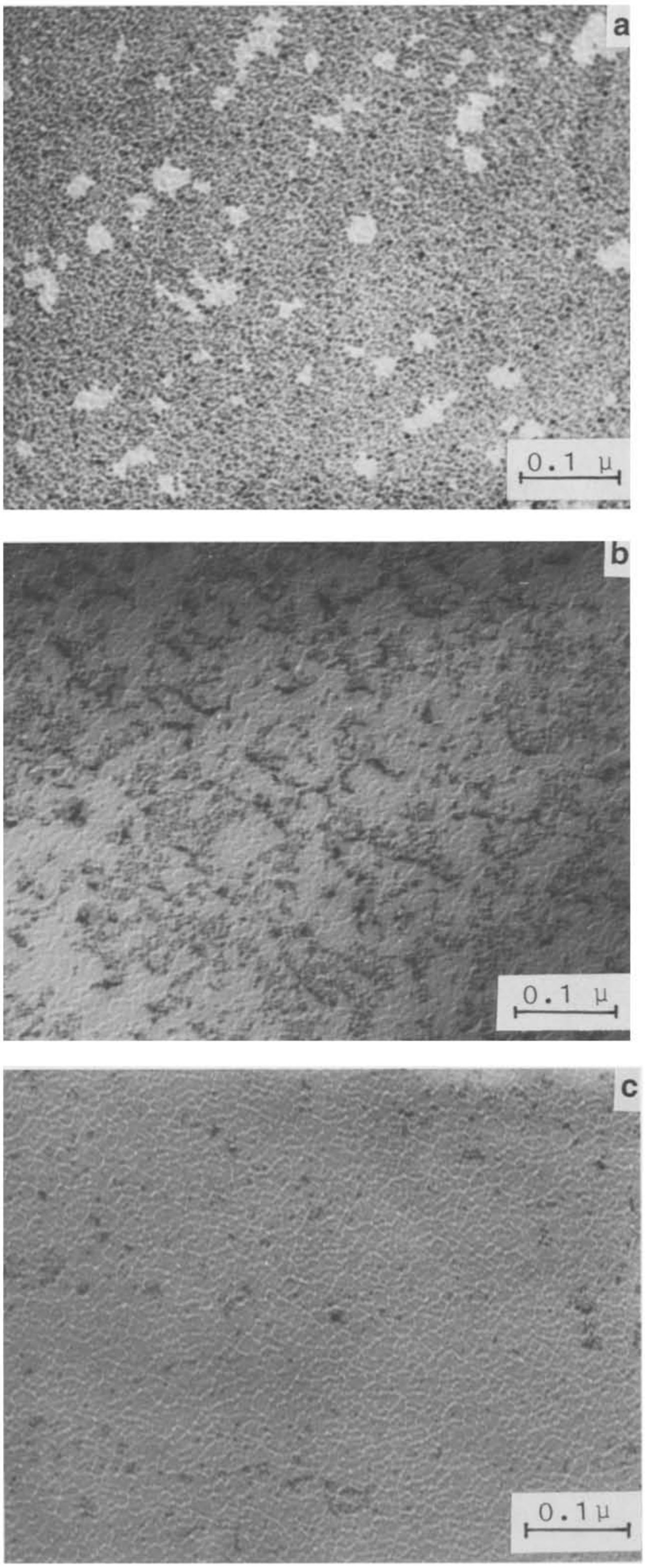

Figure 12 TEM micrographs of one-stage C–Pt replicas of the etched fracture surface of (a) DGEBA/DETA, (b) DGEBA/DETA/1% $Co(acac)_3$ and (c) DGEBA/DETA/1% $Cr(acac)_3$

that of the DGEBA/DETA sample was the least, as seen in *Figure 12*. It was also revealed that the etched area beneath the top surface (less than 10 nm in depth) is as flat as the top surface. The most severely etched surface found in the DGEBA/DETA/1% $Cr(acac)_3$ specimens might be the result of a predamaged fracture surface, since they have been fractured with the highest fracture energy. However, the possibility cannot be ruled out that $Cr(acac)_3$-incorporated epoxy resins might dissolve more easily in formic acid.

TGDDM/DDS epoxy resin systems

Curing properties. TGDDM is a high-temperature tetrafunctional epoxy resin, primarily used for aerospace applications. *Figure 13* shows the d.s.c. spectra of TGDDM incorporated with various molar percentages of $Cr(acac)_3$ or $Co(acac)_3$, and then cured with DDS curing agent in stoichiometric ratio. The higher catalytic effect of $Co(acac)_3$ than of $Cr(acac)_3$ is clearly seen in the figure, similar to the DGEBA/DETA epoxy systems shown in *Figure 3*. A single exothermic peak was found in the d.s.c. spectra of all our samples, although a second exothermic peak at lower temperature (around 160°C) was reported by Stoakley and St Clair[7] in their $Co(acac)_3$-incorporated TGDDM/DDS/Novolac epoxy systems. Obviously, the Novolac in the epoxy resin was responsible for their observed second exothermic peak.

The change of T_g of modified TGDDM/DDS epoxy resins as a function of molar ratio of their incorporated $Cr(acac)_3$ or $Co(acac)_3$ is shown in *Figure 14*. As seen in this figure, their T_g decreased with increasing percentage of $Cr(acac)_3$ or $Co(acac)_3$. However, the T_g of $Cr(acac)_3$-incorporated TGDDM/DDS epoxy resins decreased a little more. One can also see that both $Cr(acac)_3$ and $Co(acac)_3$ have lowered the T_g of their incorporated TGDDM/DDS more than that of the corresponding DGEBA/DETA epoxy systems by

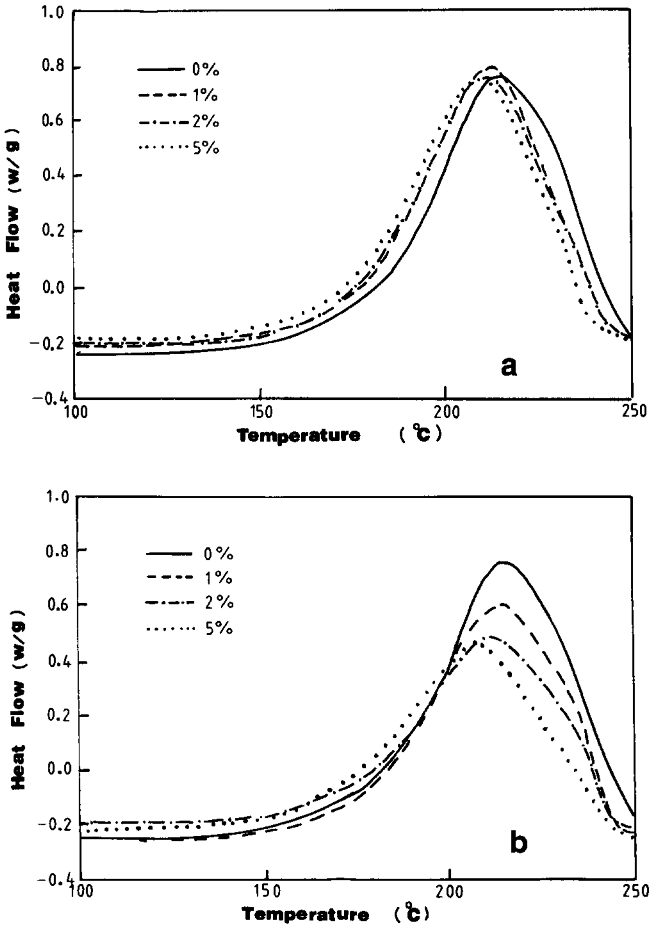

Figure 13 D.s.c. spectra of TGDDM epoxy resins containing various molar percentages of (a) $Cr(acac)_3$ and (b) $Co(acac)_3$, cured with DDS in stoichiometric ratio

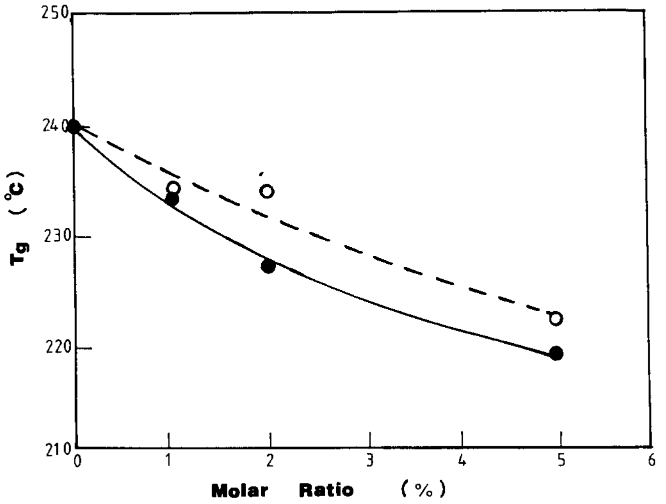

Figure 14 T_g of modified TGDDM/DDS epoxy resins as a function of molar ratio of incorporated (●) $Cr(acac)_3$ and (○) $Co(acac)_3$

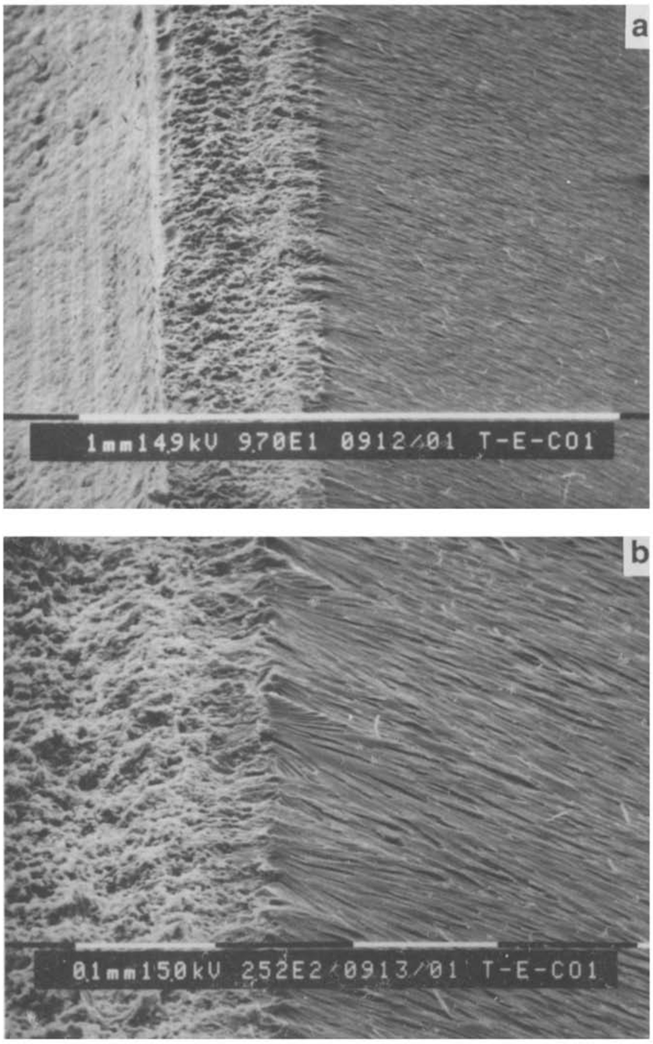

Figure 15 (a) A typical SEM micrograph of a fracture surface of TGDDM/DDS CTS specimen. (b) Magnified picture of (a)

comparison between *Figures 14* and *7*. This might be due to the curing temperature of the TGDDM/DDS epoxy resin being close to the decomposition temperature of $Cr(acac)_3$ and $Co(acac)_3$, producing decomposed debris to plasticize the epoxy resins.

Fracture toughness and morphology. The G_{Ic} value of TGDDM/DDS epoxy resins was measured as 80 J m^{-2}, much smaller than that of DGEBA/DETA. A typical fracture surface of TGDDM/DDS CTS specimens observed by SEM is shown in *Figure 15*. In general, the crack initiation region for the TGDDM/DDS epoxy system extended through to the end of the specimens. *Figure 16* shows the G_{Ic} value of modified TGDDM/DDS epoxy resins as a function of molar ratio of incorporated $Cr(acac)_3$ and $Co(acac)_3$. Similar to the DGEBA/DETA epoxy systems, $Cr(acac)_3$ has a greater toughening effect on TGDDM/DDS epoxy resin than does $Co(acac)_3$. Incorporating 1% $Cr(acac)_3$ into TGDDM/DDS epoxy resins could increase their G_{Ic} value 3.75 times, whereas incorporating 1% $Co(acac)_3$ could increase it 2.1 times. *Figures 17a–c* show SEM micrographs of the crack initiation region in the fracture surfaces of TGDDM/DDS, TGDDM/DDS/1% $Co(acac)_3$ and TGDDM/DDS/1% $Cr(acac)_3$, respectively. Again, similar to the DGEBA/DETA epoxy system, the striations in the fracture surface of TGDDM/DDS epoxy resin were denser than those in the TGDDM/DDS/1% $Co(acac)_3$ and TGDDM/DDS/1% $Cr(acac)_3$ specimens. The distance between two adjacent striations averaged from 300 data points was 2 μm for TGDDM/DDS, 3.5 μm for TGDDM/DDS/1% $Co(acac)_3$ and 5 μm for TGDDM/DDS/1% $Cr(acac)_3$ specimens. Because of the fact that the striations were marks on the fracture surface where the epoxy resins were torn off parallel to the crack growth direction, TGDDM/DDS epoxy resin with denser striations indicates that it is easier to tear and less tough than TGDDM/DDS/1% $Co(acac)_3$ and TGDDM/DDS/1% $Cr(acac)_3$ specimens. For the same reason, the higher fracture energy of DGEBA/DETA epoxy resins than TGDDM/DDS is associated with fewer striations in the fracture surface and being more difficult to tear.

TEM micrographs of one-stage C–Pt replicas of the initiation regions in the fracture surfaces of TGDDM/DDS, TGDDM/DDS/1% $Co(acac)_3$ and TGDDM/DDS/1% $Cr(acac)_3$, respectively, are shown in *Figures 18a–c*. It can be seen that the fracture surface of TGDDM/DDS specimens at 150 000 × magnification is rougher than that of DGEBA/DETA specimens. The roughness in the fracture surface of epoxy resins has been

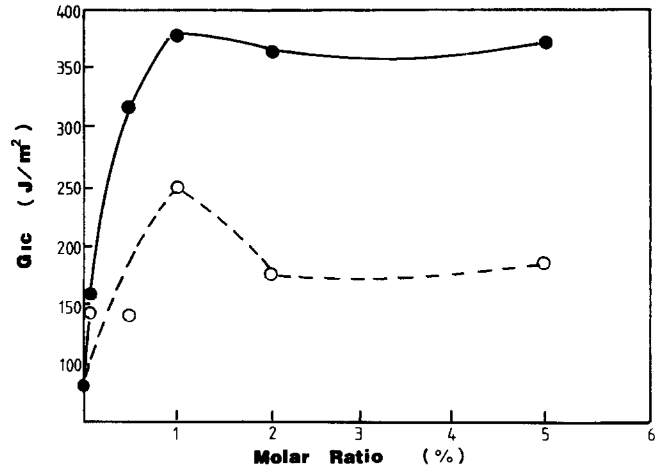

Figure 16 G_{Ic} value of modified TGDDM/DDS epoxy resins as a function of molar ratio of incorporated (●) $Cr(acac)_3$ and (○) $Co(acac)_3$

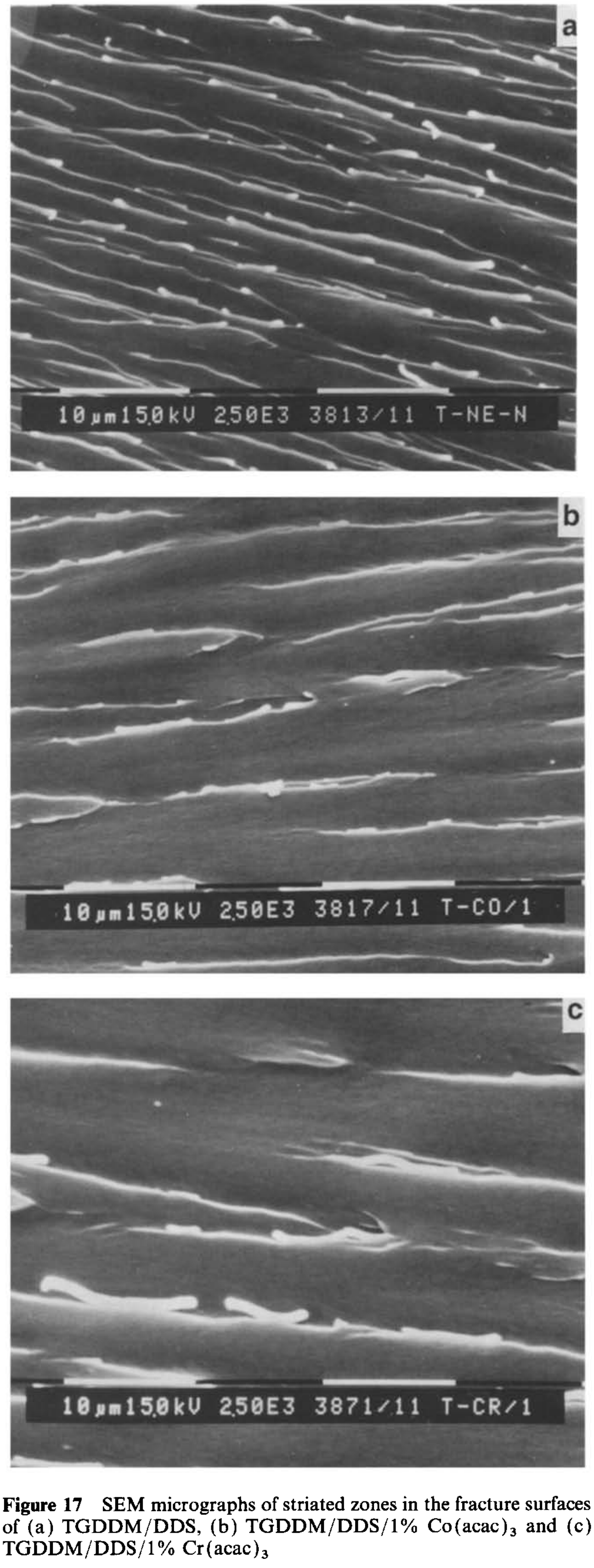

Figure 17 SEM micrographs of striated zones in the fracture surfaces of (a) TGDDM/DDS, (b) TGDDM/DDS/1% Co(acac)$_3$ and (c) TGDDM/DDS/1% Cr(acac)$_3$

interpreted as regions of high crosslink density dispersed in a lower crosslink density matrix[13]. If this were the case, the greater homogeneity in the crosslinked network of DGEBA/DETA specimens over that of TGDDM/DDS would be at least partially responsible for its higher fracture toughness.

The fracture surface of TGDDM/DDS/1% Cr(acac)$_3$ observed in TEM was quite different from that of TGDDM/DDS. The top layer of the former (less than 10 nm thickness) has been fractured into pieces as seen in *Figure 18c*. The fracture surface of TGDDM/DDS/1% Co(acac)$_3$ also showed a damaged feature in the top layer, but less severely, as seen in *Figure 18b*. This explains why TGDDM/DDS/1% Cr(acac)$_3$ specimens were the most difficult to tear and why they had taken the highest

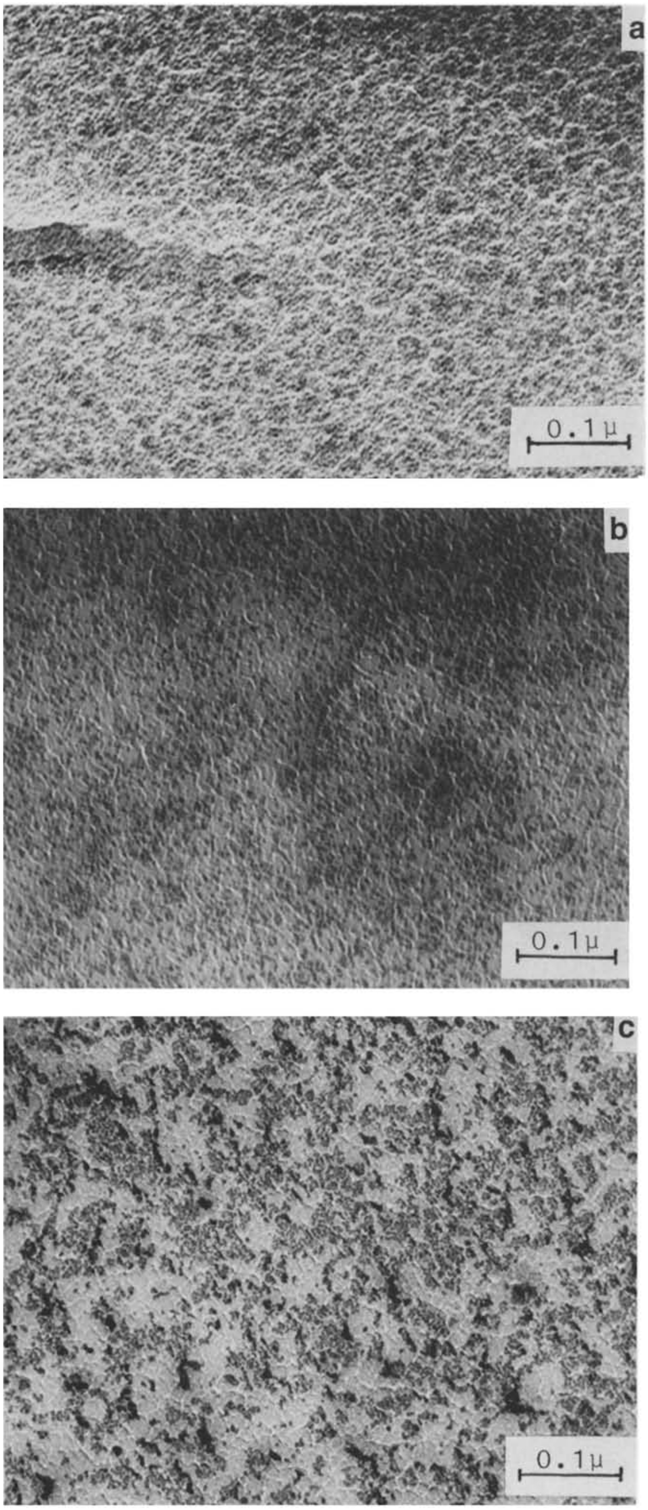

Figure 18 TEM micrographs of one-stage C–Pt replicas of the fracture surfaces of (a) TGDDM/DDS, (b) TGDDM/DDS/1% Co(acac)$_3$ and (c) TGDDM/DDS/1% Cr(acac)$_3$

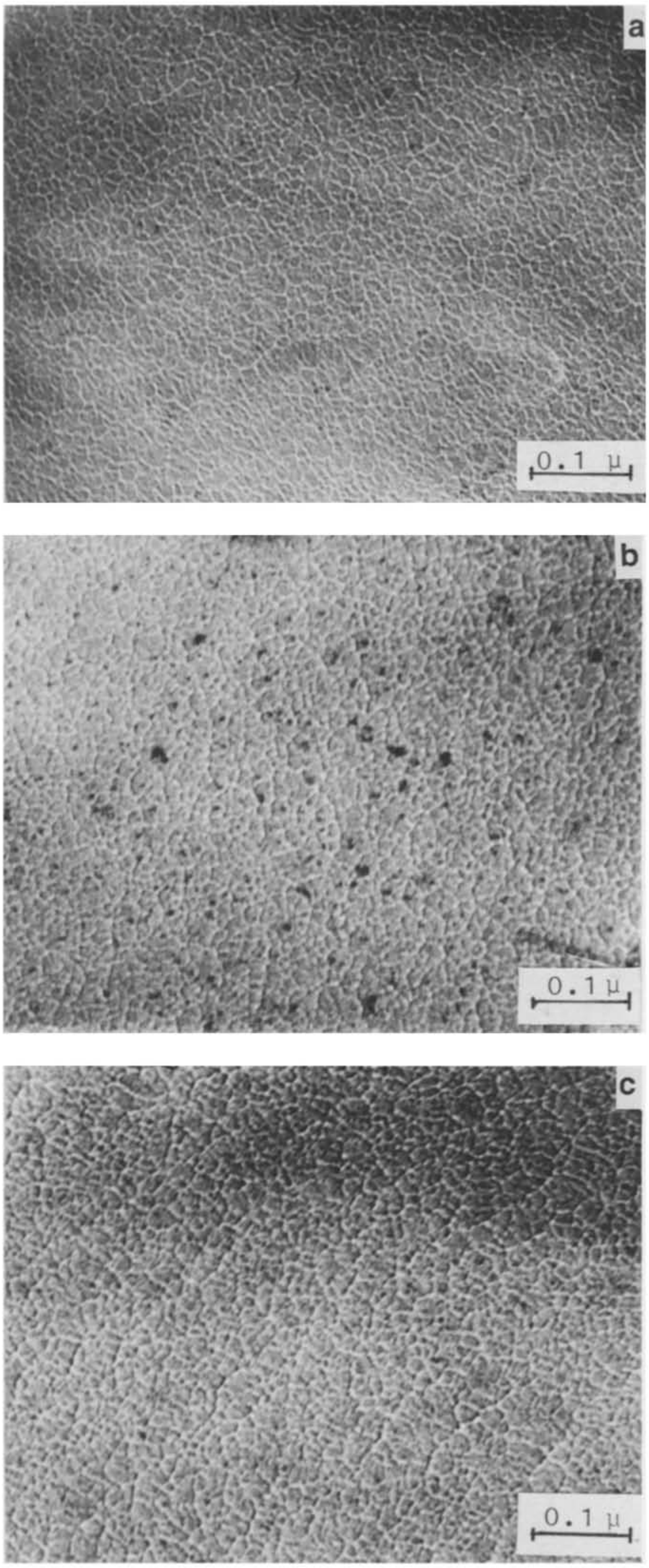

Figure 19 TEM micrographs of one-stage C–Pt replicas of the etched fracture surfaces of (a) TGDDM/DDS, (b) TGDDM/DDS/1% $Co(acac)_3$ and (c) TGDDM/DDS/1% $Cr(acac)_3$

energy to fracture among the three samples. All three samples after being etched with formic acid at room temperature for 1 h had their top layers in the fracture surface almost completely removed, as seen in *Figure 19*. The etched surfaces, having a microstructure similar to the surface beneath the top layer of the unetched fracture surface of TGDDM/DDS/1% $Cr(acac)_3$ specimens, are as flat as or even flatter than the fracture surface of TGDDM/DDS epoxy resins.

So far we have discussed the effects of incorporated $Cr(acac)_3$ and $Co(acac)_3$ on the fracture toughness and morphology of DGEBA/DETA and TGDDM/DDS epoxy resins. However, the experimental results revealed two fundamental questions. One is why the epoxy networks were fractured or etched layer by layer in less than 10 nm thickness. The other is why $Cr(acac)_3$ could provide higher toughening effects on the epoxy resins than could $Co(acac)_3$.

To answer the first question, we have studied the structure of cured DGEBA/DETA epoxy networks by wide-angle X-ray scattering (WAXS). Three peaks at scattering vectors $Q = 3.56$, 12.5 and 29.2 nm^{-1} were found in the diffraction pattern shown in *Figure 20*. It has been suggested by many researchers[14–16] that the peak observed in the Q range of 3–4 nm^{-1} is associated with a locally ordered structure in the epoxy networks, whereas the intermediate peak located at $Q = 12.5\ nm^{-1}$ is a typical amorphous halo and arises from intermolecular correlations. By using the Bragg equation to calculate the d-spacing of local ordered structure corresponding to the peak position located at $Q = 3.56\ nm^{-1}$, its repeat distance can be determined as 17.6 Å, which is the same order of magnitude as the thickness of the etched layer in the fracture surface of DGEBA/DETA epoxy resin shown in *Figure 11a*. In other words, the local ordered structure might be composed of planar networks that are packed together at a repeat distance of 17.6 Å. We considered that curing of epoxy resins started with linear growth and then branched, proceeding with two-dimensional growth. The formation of planar networks might be due to two-dimensional branched molecular chains containing considerable amounts of amine groups and hydroxy groups, which possess high polarity that might render many of them packed together before they crosslink with each other.

In order to investigate this issue further, we have cured the DGEBA/DETA epoxy specimen at room temperature in the < 1 mm gap between two plates, one of which was rotated at 550 rev min^{-1}; the device is shown schematically in *Figure 2*. Rotation has been stopped just before the

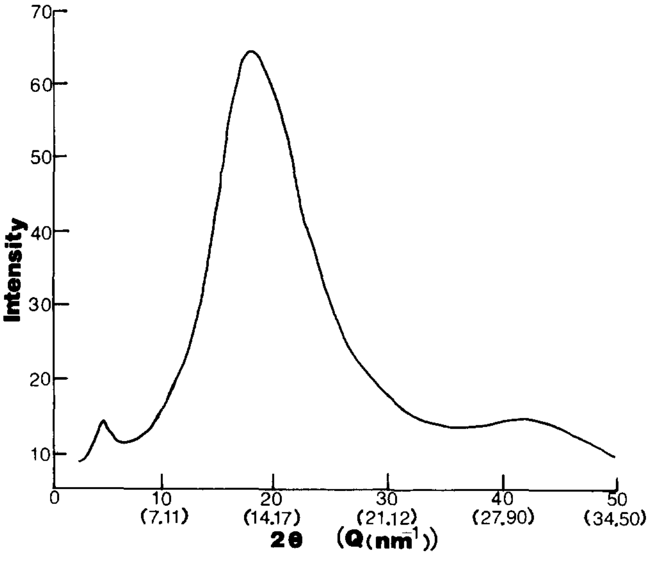

Figure 20 WAXS diffraction pattern of cured DGEBA/DETA epoxy resin

specimen vitrified. The specimen was then post-cured at 128°C for 10 h. Pre-cure under rotation was to force the molecular chains to grow anisotropically in order to facilitate packing of the branched molecular chains. The WAXS diffraction pattern of cured specimens shown in *Figure 21* revealed that the peak responsible for the local ordered structure had higher intensity, indicating that pre-cure under rotation has indeed oriented the local ordered regions.

The other fundamental question was why $Cr(acac)_3$ has higher toughening effects on the epoxy resins than does $Co(acac)_3$. No apparent chemical reaction was detected between metal complexes and DGEBA epoxy resins by i.r., u.v. or ^{13}C n.m.r. spectroscopies after they have been mixed in MEK solvent and vacuumed to get rid of the solvent at 100°C for 24 h. However, g.p.c. analysis on their mixture has shown a certain interaction between $Cr(acac)_3$ and DGEBA molecules, which was not found for DGEBA/$Co(acac)_3$ mixtures.

DGEBA epoxy resin with $EEW = 187\ g\ mol^{-1}$ has three peaks and one shoulder in its g.p.c. chromatogram shown in *Figure 22*, indicating that it was a mixture of four different molecular-weight species. The typical chemical structure of the resin is shown in *Figure 23*. It has been shown that the largest peak was contributed by DGEBA molecules with $n = 0$, whereas the middle peak, the left peak and the shoulder were contributed by such molecules with $n = 1$, $n = 2$ and $n = 3$ respectively[17]. For the epoxy resin mixed with 1% $Co(acac)_3$, its g.p.c. chromatogram was similar to that of neat epoxy resin, indicating that no interaction between DGEBA molecules and $Co(acac)_3$ was detected. However, for the epoxy resin mixed with 1% $Cr(acac)_3$, the intermediate peak was greatly reduced whereas the left peak has an additional shoulder, as shown again in *Figure 22*. Apparently, $Cr(acac)_3$ has attached to DGEBA molecules during the mixing stage, especially to the molecules with $n > 0$. By increasing the content of $Cr(acac)_3$ from 0.5% to 5% in the mixture, we were able to see the gradual decrease of intensity of the intermediate peak and the increased broadness of the left peak, as shown in *Figure 24*. In order to check further that $Cr(acac)_3$ was attached to the DGEBA molecules with $n > 0$, we have used an epoxy resin with n very close to 0 (Shell's EPON 825) to mix with $Cr(acac)_3$, and found that no apparent interaction was detected in their g.p.c. chromatograms shown in *Figure 25*.

G.p.c. results indicated that $Cr(acac)_3$ attached to the hydroxy groups in the DGEBA molecules during mixing, since the difference between DGEBA with $n = 0$ and $n > 0$ is that the latter possesses hydroxy groups. During cure of the epoxy resins, each opened epoxy group would produce one hydroxy group. It has been shown that, after the epoxy resins were cured, each incorporated $Cr(acac)_3$ was able to interact with more than one hydroxy group and hence provided an

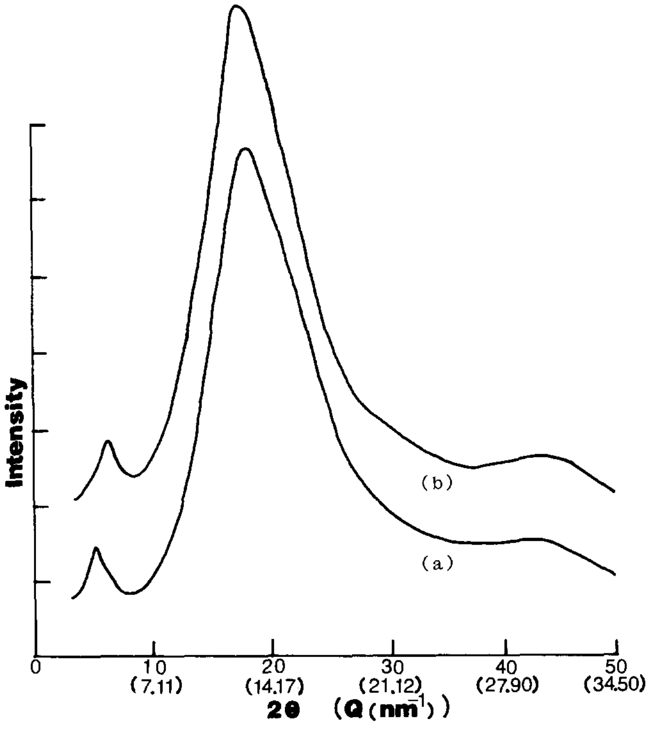

Figure 21 WAXS diffraction patterns of cured (a) DGEBA/DETA and (b) DGEBA/DETA/1% $Cr(acac)_3$ epoxy resins, prepared by pre-curing under rotation at 550 rev min^{-1} in the device shown in *Figure 2*

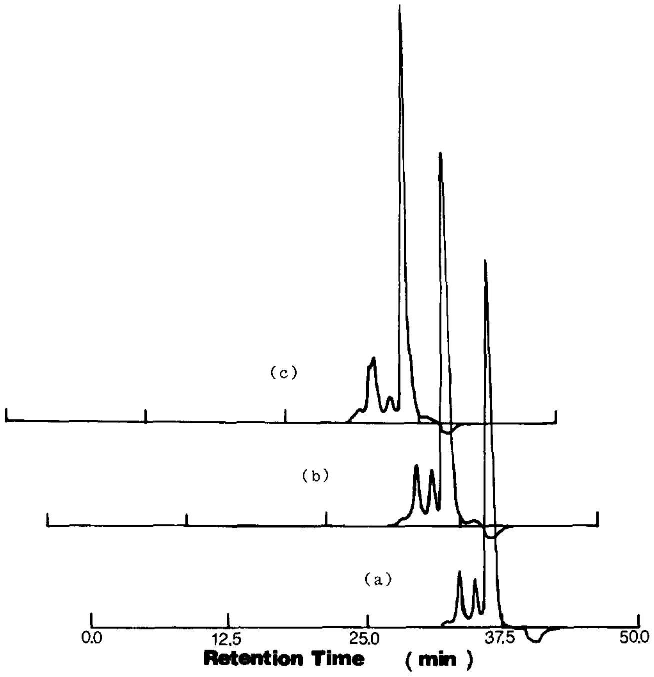

Figure 22 G.p.c. chromatograms of (a) DGEBA monomers ($EEW = 187\ g\ mol^{-1}$) and their mixtures with (b) 1% $Co(acac)_3$ and (c) 1% $Cr(acac)_3$

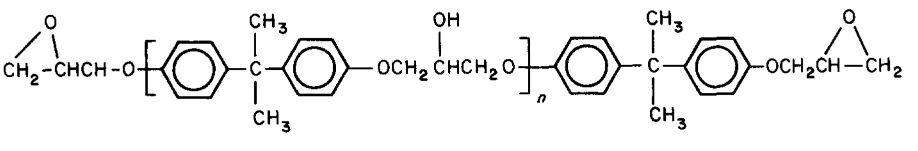

Figure 23 Typical chemical structure of DGEBA epoxy resin

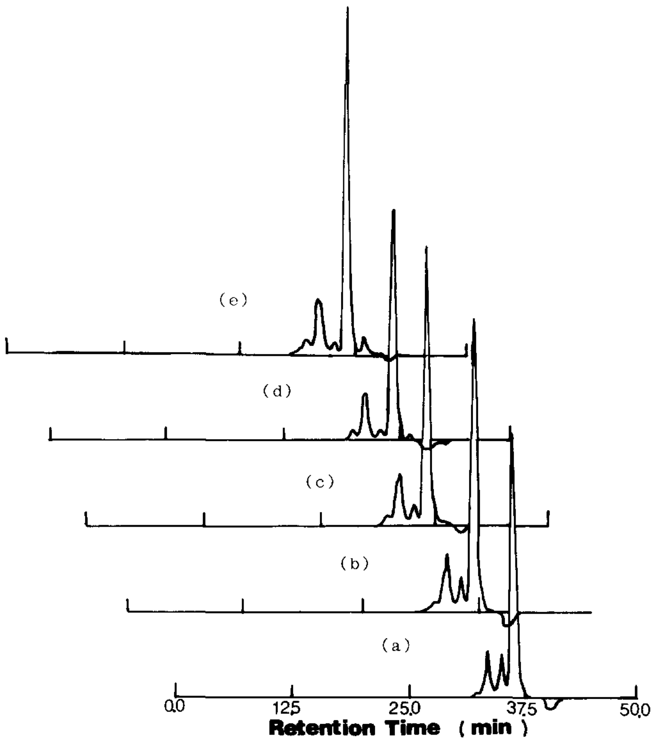

Figure 24 G.p.c. chromatograms of DGEBA monomers (EEW = 187 g mol^{-1}) mixed with various molar ratios of Cr(acac)$_3$: (a) 0.5%, (b) 1%, (c) 2% and (d) 5%

additional bonding in the epoxy networks[17]. Furthermore, the WAXS diffraction pattern of cured DGEBA/DETA/1% Cr(acac)$_3$ epoxy resin, prepared by precuring under rotation in the device shown in *Figure 2*, had the peak responsible for the local ordered structure shifted to $Q = 3.92\ \mathrm{nm}^{-1}$ from $Q = 3.56\ \mathrm{nm}^{-1}$ as shown in *Figure 21*, indicating that incorporated Cr(acac)$_3$ has decreased the repeat distance of packed networks from 17.6 Å to 16.0 Å.

During fracture of the epoxy resins, a crack usually propagates along the weakest area in the structure, which we believe is in the area between two adjacent planar networks in the locally ordered regions. As Cr(acac)$_3$ was incorporated with the epoxy resins, it reinforced the networks by interacting with the hydroxy groups and shortened the distance between two adjacent planar networks. Therefore, the fracture of its incorporated epoxy resin required higher energy than that of neat resin and frequently broke the planar networks.

CONCLUSIONS

The toughening effects of Cr(acac)$_3$ and Co(acac)$_3$ on DGEBA/DETA and TGDDM/DDS epoxy resins have been thoroughly investigated, and it was found that Cr(acac)$_3$ had better toughening effects than Co(acac)$_3$. Incorporating 1 mol% Cr(acac)$_3$ can provide the epoxy resins with the highest fracture toughness for both DGEBA/DETA and TGDDM/DDS epoxy systems. It increased 110% the G_{Ic} value of DGEBA/DETA epoxy resin and increased 3.75 times the G_{Ic} value of TGDDM/DDS. SEM investigation on the fracture surfaces showed that the epoxy resins toughened with Cr(acac)$_3$ or Co(acac)$_3$ had fewer striations in their crack initiation regions. Since the striations were marks where the epoxy resin was torn off in the crack propagation direction, fewer striations in the fracture surface of Cr(acac)$_3$- or Co(acac)$_3$-incorporated epoxy resins indicated that their resins were more difficult to tear.

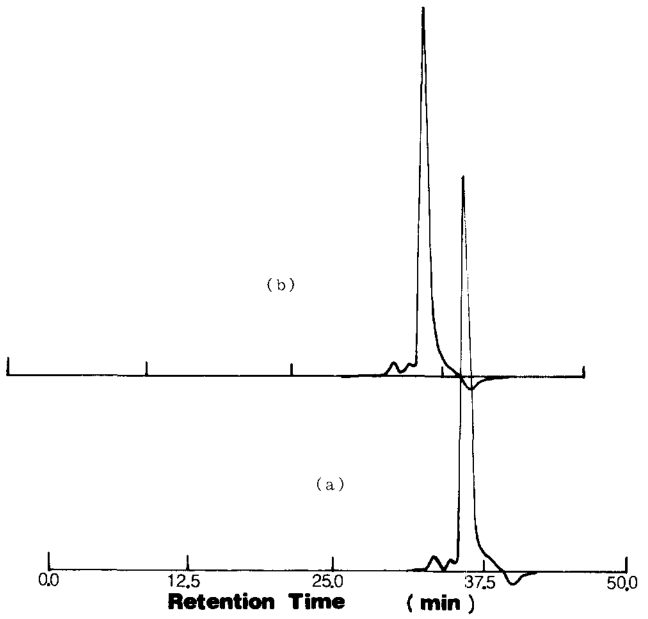

Figure 25 G.p.c. chromatograms of (a) DGEBA monomers (EEW = 174 g mol^{-1}) and (b) their mixture with 1% Cr(acac)$_3$

The fracture surface of TGDDM/DDS epoxy resins observed by TEM showed that the morphology was heterogeneous but quite uniform throughout the fracture surface, but that of TGDDM/DDS/1% Cr(acac)$_3$ had their top layer of fracture surface (less than 10 nm thickness) fractured into pieces. The damaged fracture surface of the latter explained why it needed higher energy to fracture than the former and was more difficult to tear. Although DGEBA/DETA epoxy resins incorporated with 1% Cr(acac)$_3$ did not show a similar damaged fracture surface, its top layer of the fracture surface was easier to remove by etching with formic acid than that of the neat resins.

According to the g.p.c. chromatograms of DGEBA mixed with Cr(acac)$_3$ and Co(acac)$_3$, Cr(acac)$_3$ was capable of interacting with hydroxy groups and reinforcing the epoxy networks but Co(acac)$_3$ could not. The WAXS diffraction patterns of cured DGEBA/DETA epoxy resins revealed that the resin networks contained some local ordered structure, which might be formed by the repeat packing of planar networks. The repeat distance was measured as 17.6 Å, the same order of magnitude as the top layer of their fracture surface. The incorporation of 1% Cr(acac)$_3$ shortened the repeat distance of local ordered structure, which we believe to be the result of interaction with hydroxy groups in the resin networks.

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